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1 Abstract

Biogas production is becoming significantly viable as an energy source for replacing fossil-based fuels. The further development of the biogas production process could lead to significant improvements in its potential. Tte improvement of anaerobic digestion detection technologies is the cornerstone to reach higher methane productivities and develop fully automatized processes to decrease operational costs. New sensors are requested to automatic obtain a better interpretation of the complex and dynamical internal reactor environment. This will require detailed systematic detection in order to realise a near-optimal production process. There is currently a disparity between the complexity of anaerobic digestion, and on-line detection. By improving the durability, sensitivity and cost of dissolved H_2 sensor technology, further understanding of the anaerobic digestion process may allow the prevention of process failure. Furthermore, the detection of dissolved H_2 directly in the liquid phase would drastically reduce the time for distinguishing an imbalance in the microbial community. The emergence of surface plasmonic resonance (SPR) sensing with optical fibres coupled with the H_2-sensitive metal palladium, allows detection of dissolved hydrogen in liquid. By implementing these SPR sensors into anaerobic digestion, improvements to the biogas production process, even at small scales, may be achieved by guided the process in the optimum direction, avoiding the collapse of the biological process. This review intends to assess the feasibility of on-line, cost-effective, rapid, and efficient detection of dissolved H_2 in anaerobic digestion by SPR.

2 Introduction

One route to production of renewable, clean energy is through biogas production, where biogas is derived from organic waste materials. The production of biogas is achieved through the anaerobic digestion (AD) of the organic waste materials by various microorganisms (1). Another route to renewable, clean energy is the so-called Power-to-Gas route, where surplus renewable electrical energy is used to produce H_2 by electrolysis. However, H_2 utilisation is facing unsolved bottlenecks related to H_2 transport and storage. An attractive alternative to H_2 distribution is to convert H_2 to methane in a biological methanation process (2,3). Methane has a much higher volumetric energy content than H_2 and thus a lower storage transport cost, and can be distributed in existing natural gas infrastructure (4). By utilising the methanation process, H_2 can be used to reduce the CO_2 in the biogas produced (2,3). A promising approach is to input H_2 to the biogas reactor such that the methanation takes place within the reactor (2). However, increasing the concentration of dissolved H_2 in the reactor can inhibit the production of biogas and accumulate VFAs, and in the worst case cause the whole biological process to collapse (5).

Due to the complexity of the biogas production process, it is not always straight-forward to determine the state of the AD process from measuring the chemical variables within the digester (1). Despite this, the hydrogen content of produced biogas is a very sensitive indication of imbalance between microbial groups within the digester (6–8). Although hydrogen is straightforward to measure in the gas-phase, dissolved hydrogen in the liquid phase is considered more appropriate as the liquid to gas mass transfer of hydrogen introduces a significant delay in detection (9). Therefore, dissolved H_2 is recognised as a better approach to an early warning indicator and an excellent complement to VFA monitoring (5). Dissolved H_2 concentrations are, therefore, required control parameters for biogas production monitoring and utilising H_2 for further methanation of CO_2 (2,3). It is essential that dissolved H_2 be monitored closely to gain an understanding of the current biological process within the digester.

Cost-effective sensor technologies for monitoring and analysis of H_2 within the reactor are crucial for improving efficiency, productivity and cost of biogas production in many plants. There are many methods for achieving monitoring of a variety of parameters within bioreactors. These may rely on sample extraction, but in some cases, the sensor can be

interfaced directly with the internal environment of the bioreactor. Despite this, there are still improvements required to make ideal sensors for the measurement of dissolved H_2 within the biogas production process. Ideally, a monitoring system must have cost-effective, accurate, specific, stable and sensitive sensors, which can send data to software programs for analysis. This data can then be computationally analysed, allowing the correlation of the sensor data to a specific parameter or process model. Furthermore, with the increase in small-scale plants, there is a significant demand for sensor technologies that do not have an associated high cost.

In this review, contemporary sensor technologies that can combine AD with on-line sensor technologies focusing on dissolved H_2 are discussed and compared to current industry methods. The contemporary technologies presented have the potential for improving the efficiency, economic costs and productivity of biogas plants, as well as allowing on-line dissolved H_2 monitoring to facilitate H_2 injection for methane upgradation.

3 Sensors Requirements for State of an Anaerobic Digester Determination

There are distinctive ways that sensors can be fused into the AD plant to satisfy the on-line observing prerequisite. The sensors utilized for estimations of factors inside an AD plant can require the extraction of digestate from the bioreactor, filtration and external sampling (at-line sensor), the sensor to be located inside the digester (in-line sensor), or to be removed from the digester and sampled in a lab (disconnected sensor) (10).

The in-line sensors must be impervious to pressure (somewhat above atmospheric pressure) and temperature (somewhere in the range of 35°C and 55°C), as well as having the capacity to be cleaned. Also, they must be significantly impervious to obstruction by fouling. Ideal sensors must provide proper detection quality, having high precision, specificity and sensitivity. The collected information must then automatically be processed and used in the supervision system. The figured estimations should deliver consistency and be steadiness despite changes in medium changes in biological or chemical contents. In practice, the benefits of the sensor in terms of increasing process reliability and efficiency must be compared to its price, including manpower requirement for human intervention (setup, calibration, cleaning).

For live, on-line detection of an AD plant to be valuable, the reaction time of the sensors is a critical trademark (10). Even though the delay of measurements is explicit to every sensor and application, the time required to acquire an outcome must be small (< 10 minutes) concerning the biological dynamics within the digester. All the more explicitly, the time required to acquire a sensor outcome will depend altogether on the retention time of the AD reactor, duration of analysis and the dead volume of the filtration framework utilised. Also, it must be a lot quicker than the time required for the gathering of H_2 to happen to distinguish and avoid a stress event. With this in mind, the sensor framework must be tailored to the procedure with satisfactory sampling locations. Otherwise, the low effectiveness of the process control will occur (11).

The location of the sensor inside the digester is fundamental, as the digester can be homogeneous or inhomogeneous. This depends mainly on the feedstock type, process size and AD technologies. Also, there are AD methods that have intended inhomogeneous chemical gradients inside the reactor (e.g., up-flow anaerobic sludge blanket (UASB) & fluidised bed reactors), and this is exacerbated with the expansion of reactor size. Despite this, if the digestate is homogeneous, the sensor can be set anywhere inside the bioreactor, and the signal from the sensor will represent the real state; however, if it is significantly inhomogeneous, several sensors might be required to decipher the state of the digester completely.

There are three primary phases (solid, liquid and gas), inside an AD plant. These phases have diverse properties, factors and prerequisites when considering in-line sensors. The liquid phase of the anaerobic digester is an intricate blend of different microorganisms, substrates, nutrients, products, metabolites and dissolved gases. Because of the diffusion rate of components from liquid to gas, it is attractive to make estimations specifically from the liquid phase of the digester. This can decrease the lag time between changes in the AD biological dynamics and identification of these changes.

4 Traditional H_2 Detection

4.1 Dissolved H2 detection

Dissolved H_2 produced in AD has long been recognised as an early warning indicator and an excellent complement to VFA monitoring (5,9). Additionally, the *in situ* hydrogen injection into the anaerobic digester is a promising process aimed at increasing the biogas methane content, at the expense of the CO_2 content. It has been hypothesised that adding hydrogen directly into the anaerobic digester may change microbial community composition promoting hydrogenotrophic methanogenesis pathways (12). This enhances the biological production of methane by 20-40% (2,13), potentially achieving a purity of up to 90% (12,14–16) when combined with *ex situ* upgrading. This allows existing biogas plants to be utilised for H_2, eliminating the need for hydrogen storage (which can be of safety concern) (17). Despite this, dissolved H_2 can potentially inhibit production of methane, and in the worst case cause the whole biological process to collapse (5). Moreover, injection of H_2 to a level exceeding a 4:1 stoichiometric ratio between H_2 and CO_2 tends to deplete CO_2 resulting in the rise of pH (13), and inhibiting the autotrophic hydrogenotrophic methanogenesis process (18). Furthermore, the oxidation of acetate towards methane production is only thermodynamically favourable when the partial pressure of H_2 is below 74 Pa (19,20). Therefore, dissolved H_2 must be monitored continually, especially if H_2 is directly injected into the anaerobic digester for methane upgradation.

Since the critical concentration of dissolved H_2 is only 74 Pa (19,20) and difficult to measure, the concentration of dissolved H_2 in anaerobic biogas production is currently calculated from a gas fraction of H_2 detected in the gas phase of the digester. However, due to the limited H_2 mass-transfer coefficient, there is a significant time delay between an increase in H_2 concentration in the liquid and an increase in the gas phase of the digester. Such time delays represent a severe limitation for optimal process control (5,9). Extraction techniques designed for off-line dissolved H_2 monitoring are time-consuming and not an option for the rapid process control desired. Other techniques based on the transfer of H_2 from the liquid through a gas-permeable membrane followed by gas phase quantification (gas chromatography or mass spectrometry), are considered too sophisticated and expensive for on-line monitoring. Therefore, there is a definite need for an effective, reliable, and cost-effective sensor for continuous on-line monitoring of dissolved H_2 in anaerobic bioprocesses.

4.1 Gas-Phase Detection

Detection of H_2 gas in the headspace of the anaerobic digester is straight-forward to measure but is delayed significantly due to the mass-transfer coefficient of H_2. Therefore, the main

drawback of the detection in the headspace is that sudden changes in dissolved H_2 levels will not be detected for some time, and, therefore, process failure could occur before any signals of an H_2 increase are detected. Despite this, membrane-covered Clark-type electrodes can be adapted to measure H_2 in the headspace of the reactor, with negligible biofouling of the membrane occurring when in gas-phase. Thermal conductivity sensors like those provided by BlueSens (BlueSens, Germany) can also gauge the concentration of H_2 gas in the headspace. These sensors use a small heated filament to detect thermal conductivity of the gases in simple gas mixtures, allowing the determination of the percentage of specific gases of interest within a mixture.

Palladium metal oxide semiconductor (Pd-MOS) sensors have also been studied for their suitability for H_2 detection in the gas phase of AD (21). The palladium can become palladium hydride in the presence of H_2, a rapid and reversible reaction that can alter the conductivity of the metal and used to determine the ppm of H_2. Alternatively, gas chromatography (GC) instruments equipped with thermal conductivity detectors can be used to determine H_2 (8). GC is a very accurate method of H_2 detection in the gas phase and is regularly used as a reference measurement technique for all other H_2 detection methods.

4.2 Liquid-Phase Detection

H_2 can be detected using a membrane-covered Clark-type electrode (22) in the liquid phase as well. There are extraction and H_2 permeable membrane methods designed for dissolved H_2 monitoring within the digester, but these can be expensive and time-consuming processes. The membrane requiring Clark-type electrodes can be used for on-line monitoring of dissolved H_2 in the liquid-phase, which relies on the oxidation of H_2 at a Pt electrode and dissociation of molecular hydrogen at a Pd electrode (23,24). Unfortunately, these are prone to biofouling on the membrane surface. Once biofouling occurs, the measurements from this type of electrode are mostly unreliable, and, therefore, the membrane must regularly be replaced to avoid this. So far all reported electrochemical sensors for H_2 detection suffer from membrane fouling resulting in a short lifetime, low selectivity and low signal-to-noise ratio (24). Although these Clark-type sensors can operate at room temperature, temperature fluctuations must also be taken into account to maintain correct O_2 and H_2 calculations (25).

Measurements of dissolved hydrogen can also be performed using hydrogen microsensors like those provided by Unisense (Unisense A/S, Denmark). Microsensors allow H_2 to diffuse from the internal liquid phase of the anaerobic digestor through a silicone membrane to a

platinum anode that is polarized against an internal reference. The current between the palladium electrode and the reference is linearly indicative of the dissolved hydrogen at the tip of the sensor. The current change is in the picoamp range and is measured using a picoammeter. An alternative method for dissolved H_2 detection was described by Björnsson et al. (2001). Here, a liquid-to-gas membrane was utilised to extract dissolved H_2 from the liquid phase, through a Teflon membrane placed in the internal environment of the anaerobic digester. The H_2 was then detected using a Pd-MOS sensor (26).

4.3 Remarks

The methods outlined here suffer from disadvantages including sample preparation, contamination and biofouling. GC is a real proven alternative at very high accuracy, but requires advanced systems for auto-sampling, transfer of the sample and filtering, and requires a significant amount of time to obtain a measurement. Forms of ultrafiltration are required for liquid phase detection to produce a clear particle-free sample for GC and electrochemical detection methods. This filtration will result in biofouling in the long term, a property that must be considered when using such methods for detection in the liquid phase.

Measurements undertaken in the gas phase of the reactor have limited issues with biofouling of filtration systems; however, the presence of H_2S in the biogas massively reduces the sensitivity of the sensor systems (21). Additionally, the mass-transfer rate of H_2 from the liquid phase to the gas phase is prolonged, resulting in significant delays when detecting H_2 spikes in the AD process (9).

5 Software Sensors

Using mathematical approaches, information provided by on-line sensor systems can be extended. The two strategies for achieving this are based on methods of data analysis and the representation of the dynamics of the plant by mathematical models.

5.1 Observers

The incorporation of software sensors with on-line sensor systems allows the prediction of the biological process state by estimating non-measured variables. In the case of dissolved H_2 measurements, estimations of the dominating microbial processes within the reactor can be made. Additionally, software sensor systems are a vital supporting component of closed-loop central strategies. These approaches are also known as state observes or state estimators, and

have a large amount of theoretical background. Assimilation of the real-time on-line measured variable(s) can be combined with the theoretical knowledge base of the AD process through a mathematical model allowing the prediction of variables that have a low frequency or no sampling. Depending on the desired accuracy, the frequency of sampling, sensor information quality and frequency of sampling, different strategies for the design of an appropriate software sensor can be applied.

Linear frameworks, or extensions thereof, are popular approaches to software sensing. The most known algorithms for achieving software sensors are based on extended Kalman filters (EKF) and extended Luenberger observers (ELO) (27). Despite their popularity, the required local linear approximation of the process model reduces the certainties of the stability and convergence properties for wide operating ranges. Furthermore, perfect knowledge of the model and its parameters are assumed by these algorithms, allowing the approach to be sensitive to any inaccuracy within the model parameters.

To reduce the dependency of the algorithms on parameter uncertainty, different strategies have been developed by using the mass balance information from the reactor as the base of the estimation scheme. Although mass balance only represents the process partially, it can robustly deal with any missing information. Moreover, estimates of kinetics for some processes in the model can be achieved with the support of gaseous flow rates using asymptotic observers (28). These methods can achieve a linear observer by relying on changes of variables cancelling nonlinear terms within the process (29). However, the dilution rate controls the convergence rate when utilising asymptotic observes. Simultaneous estimating of model parameters and the state of the process can be performed with adaptive observers (30). Alternatively, using the process model and its known parameters allows the tailoring of nonlinear observers with the nonlinearity of the process accounted for by the algorithm (31). A significant limitation of the implementation and calibration of such observer algorithms is their inherent complexity.

Internal observers offer a flexible method by providing guaranteed estimate intervals where the state of the variable lies, avoiding reconstruction of precise numerical values (32,33). This has been observed successfully for use in AD (34,35). Due to the uncertainty of concentrations in the influent, this parameter is inherently difficult to use to estimate the process accurately. To overcome this, an algorithm that simultaneously estimates the influent concentrations using both input and state observers has been shown to alleviate this drawback

(36). Further development of these observers has resulted in their extension to handle spatial distributions within the anaerobic digester (37,38).

6 Emerging SPR Sensor Technologies

More recently, various optical sensor principles have been proposed for H_2 monitoring (39–51). Sensors based on the H_2 uptake in palladium appear particularly promising. The volume expansion of palladium films or nanoparticles caused by metal-hydride formation can be measured very accurately using optical techniques (39,40,44,47,49,50). Additionally, the surface plasmon resonance (SPR) of gold (when coupled to palladium in a layer stack), can be measured accurately, with the plasmon resonance frequency being modulated by the hydrogenation of the palladium layer (43,45,48).

SPR sensors exploit the interaction of incident electromagnetic waves with the oscillation of the plasmon wave of a material (e.g., gold). When the momentum of incident electromagnetic waves matches the momentum of the surface plasmon waves in the gold, the electromagnetic waves are coupled to the plasmon wave and are diminished (FIG???). The frequency of the plasmon wave can be altered by changes in the materials used, therefore changing the wavelength of incident electromagnetic waves absorbed. An example of this is the use of a bare, cladding-less optical fibre with a gold and palladium layer-stack (Fig). The incident electromagnetic wave interacts with the plasmon wave on the surface of the gold layer. Furthermore, this plasmon wave can be modulated by changes in the permittivity of the gold.

By adding an H_2-sensitive layer of palladium, the formation of palladium hydride effects the electrical field of the gold, changing its permittivity, and changing the momentum of the surface plasmon resonance of the gold. The interaction of the incident electromagnetic waves with the gold will be changed, causing different electromagnetic waves to be diminished. Using spectroscopic methods, this will culminate in a shift in apparent absorption of electromagnetic waves as a consequence of H_2 presence.

In order to engineer an SPR-based sensor with palladium as the sensing material for use in the liquid phase of an anaerobic digester, the thicknesses of the gold and palladium layers, and the incident angle of the light to the layers must be considered. Using a straight-forward model accounting for the refractive indexes of the silicon optical fibre, gold, palladium and water, a considerable variation in sensor ability is observed as a function of the incident angle

(FIG). This is also apparent with varied thicknesses of the two metal layers (FIG). To achieve a dissolved H_2 sensor with high sensitivity and high signal using only gold and palladium metal layers, an incident angle of XX, with metal thicknesses of XX of gold and XX of palladium is required. Although the thickness of the metal is straight-forward to achieve with sputtering deposition techniques, the angle of incidence requires further design considerations.

The metal layers can be deposited on the side surface of the fibre. Increases in the incident light angle can be performed on such designs by placing the optical fibre in a d-loop (Fig), or by using a Bragg grated fibres (Fig). This will allow the incident light angle to be optimised for coupling of the electromagnetic wave to the SPR wave of the gold layer. Alternatively, the metal layer stack can be deposited on the end-tip of a fibre, acting as a mirror (Fig). With the use of a multimode fibre, this will allow the electromagnetic wave to achieve coupling with the SPR wave of the gold layer. Furthermore, the metal layer stack could be deposited onto a transparent patch and installed on the internal space of the reactor behind a glass window. Probing of the sensor patch would then be achieved using an external optical fibre, reducing complexity and cost.

7 Calibration of SPR Sensors

With using palladium as the sensing material, the selectivity for hydrogen is very high. Therefore, calibration can be achieved straightforwardly by use of GC measurements of hydrogen concentration in the liquid phase.

Before a palladium-based SPR sensor can be utilised, the consistency and accuracy of the sensor must be confirmed. Different SPR sensor datasets must be comparable to establish successful data analysis. A variety of pre-processing methods can be applied to the data sets to achieve this. Some examples include deviation (52), filtering (53) normalisation, standardisation, centring, weighing and scaling (54) of the data sets. Pre-processing is a powerful and sensitive component in data analysis (55), where consideration of the chosen method is required depending on the type of data used. The exclusion of irrelevant data is also a pre-processing method that is essential. This can be achieved by normalisation or baseline subtraction/correction. Matching of the data set to known dissolved H_2 concentrations determined by GC can then be performed.

8. Promising Perspectives of SPR Sensors in AD

SPR sensors are advantageous as they can also be applied to other variables revealing the internal state of the complex anaerobic process. Acetic acid is a VFA that can be produced during certain stages within the AD of biomass. At high concentrations, it will inhibit the activity of many microorganisms within the digester (REF NEEDED). Using SPR technologies, measurements can be made of acetic acid with the receptor dye aluminium phthalocyanine chloride deposited on a layer of gold (56). This design has been shown to sense acetic acid in a liquid environment (56), suggesting its adaptation into AD may provide an accurate only measurement of acetic acid.

By utilising colloidal copper nanoparticles, detection of ammonia concentrations have been observed utilising SPR (57). By suspending colloidal copper nanoparticles in a solgel on a transparent disk behind an observation window within the digestor, direct measurements of ammonia levels would be possible by external probing of the sensor disk with an optical fibre.

Methane concentration is usually measured in the gas-phase of the digester; however, it is also possible to measure this variable within the liquid-phase of the digester. By depositing a layer of modified polydimethylsiloxane (PDMS) polymer that contains cryptophane-A molecules as the receptor, on top of a layer of gold, methane may be detected using SPR (58). This detection is due to the selective, yet reversible, affinity of cryptophane-A to methane.

The H_2S must be removed from the exhaust gases by bio-filtration methods. It is imperative that the post-filtration gas has no H_2S component, and therefore, this gas must be monitored continuously. Titanium oxide is known to react with H_2S, producing titanium sulphide. This reaction has been observed to cause a change in the resonance frequency of the surface electrons of silver (59). The resonance can then interfere with incident light, as a function of the H_2S concentration in the gas.

Although these variables have been detected using developed surface plasmon detection techniques, they are all yet to be adapted for utilisation in an anaerobic digester.

9 Perspective and Challenges for the Developments of SPR Sensors

The main limitations for palladium-based SPR sensors detecting dissolved H_2 in an AD are palladium poisoning by H_2S, biofouling and the chemical complexity of the digestate. Moreover, the repeatability of the data from the sensor in a specific digestor may change as a result of influent changes, and the comparability between different digestors with different feedstocks may also be a challenge. This can be due to a variety of reasons were certain unknowns within a complex mixture affect the dissolved hydrogen detection of the palladium-based SPR sensor.

H_2S is produced in small quantities in AD and has a negative effect on the sensitivity of palladium to H_2. Interferences of H_2S to palladium is partly reversible, but to some extent, it is irreversible (21). This has to be considered when developing a mathematical model for the sensor, as the level of poisoning will have some dynamic trend due to H_2S poisoning being partly reversible. Sample preprocessing is also possible by significantly increasing the pH of the sample to remove H_2S; however, this is not desirable as it adds another step to the detection of H_2.

As with many sensor systems placed inside the liquid phase of an anaerobic digestor, biofouling is a real limitation. There are plenty of methods for filtration of samples available that significantly reduce biofouling on the sensor at the cost of filter biofouling. An alternative is to utilise thin non-stick films of XXX on top of the palladium layer, to limit fouling of the sensor. Additionally, by allowing the sensor patch to be replaceable, the sensor could easily be replaced routinely without replacing any of the other components within the sensor setup.

Despite this, the selectivity of palladium for H_2 in such a complex mixture allows many variables within the digestate to be ignored by this sensor. Therefore, the ability for the sensor to detect a rapid rise in dissolved H_2 (irrespective of providing an entirely accurate concentration measurement), would allow rapid altercations to be made to avoid biological inhibition and potential biological process collapse. This will give the controller of the plant valuable time to rectify the biological process, by eliminating the delay in H_2 detection in the gas phase due to the slow mass transfer of H_2 between liquid and gas phases.

Optically-based SPR sensors integrated directly into the AD would result in rapid on-line dissolved H_2 detection within the liquid phase. Direct integration of these sensors (whether directly placed within the reactor, or behind an observation window), and negligible time

required to achieve sensor-H_2 interactions, will allow instantaneous measurements of the dissolved H_2 within the anaerobic digester. The development of an on-line sensor system based on SPR sensors for detection of dissolved H_2 for use in AD, coupled with automated post-treatment of the sensor data sets is a realistic alternative to traditional H_2 detection methods as.

10 Concluding Remarks

Current AD plants require sensor advances that permit the estimation of dissolved H_2 on-line, not only in large-scale plants but in small scale plants also. These advances will give the operators of AD plants the possibility to acquire not only a higher comprehension of the perplexing dynamics inside the AD plant but additionally foresee the heading of the reactor. Traditional variable estimations required extensive and sophisticated instrumentation. Additionally, with difficult extraction and preparation, experts are required leading to increased expenses. These costly, for the most part, off-line procedures are highly accurate, albeit typically do not depict an altogether precise display of the interior AD plant condition due to the potential time delay in obtaining the information. New sensor frameworks for detecting the internal dissolved H_2 condition of an AD plant must most likely show high sensitivity, specificity and precision while keeping up the practicality of an on-line information stream.

New sensor frameworks may expect parts to be disposable (e.g., SPR sensor patches); however, they must be able to achieve comparable detection attributes between disposable parts. The lifetime of such sensor segments like the sensor patches might be short in traditional terms; however, must be low-cost so they can be replaced as required. These sensors must be simple, small and isolated to encourage this. SPR optical-based sensor advances for liquid phase dissolved H_2 detection can fulfil the necessities as future on-line biogas sensors, and will fundamentally avoid the identification delay as seen with traditional gas-phase detection.

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